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Approved for use through 03/31/2012. OMB 0651-0016  
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

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**PETITION TO ACCEPT UNAVOIDABLY DELAYED PAYMENT OF  
MAINTENANCE FEE IN AN EXPIRED PATENT (37 CFR 1.378(b))**Docket Number (Optional)  
13332/16Mail to: Mail Stop Petition  
Commissioner for Patents  
P.O. Box 1450  
Alexandria VA 22313-1450  
Fax: (571)273-830008/24/2010 DALLEN 00000009 110600  
01 FC:1599 1600.00 DA

6149782

NOTE: If information or assistance is needed in completing this form, please contact Petitions Information at  
(571) 272-3282.Patent Number: 6,749,702Application Number: 09/010,822Issue Date: June 15, 2004Filing Date: January 22, 1998CAUTION: Maintenance fee (and surcharge, if any) payment must correctly identify: (1) the patent  
number (or reissue patent number, if a reissue) and (2) the application number of the actual  
U.S. application (or reissue application) leading to issuance of that patent to ensure the fee(s)  
is/are associated with the correct patent. 37 CFR 1.366(c) and (d).

Also complete the following information, if applicable:

The above-identified patent:

☐ is a reissue of original Patent No. \_\_\_\_\_ original issue date \_\_\_\_\_;  
original application number \_\_\_\_\_  
original filing date \_\_\_\_\_☐ resulted from the entry into the U.S. under 35 U.S.C. 371 of international application  
\_\_\_\_\_ filed on \_\_\_\_\_**CERTIFICATE OF MAILING OR TRANSMISSION (37 CFR 1.8(a))**

I hereby certify that this paper (along with any paper referred to as being attached or enclosed) is:

(1) being deposited with the United States Postal Service on the date shown below with sufficient postage as first class  
mail in an envelope addressed to Mail Stop Petition, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-  
1450 OR(2) transmitted by facsimile on the date shown below to the United States Patent and Trademark Office at (571) 273-  
8300.August 19, 2010

Date

/Daniel G. Harris/

Signature

Daniel G. Harris

Typed or printed name of person signing Certificate

(Page 1 of 4)

This collection of information is required by 37 CFR 1.378(b). The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Mail Stop Petition, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

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## OFFICE OF PETITIONS

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212 425 5288

P.003/021

AUG 19 2010

PTO/SB/85 (03-09)

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## 1. SMALL ENTITY

☐ Patentee claims, or has previously claimed, small entity status. See 37 CFR 1.27

## 2. LOSS OF ENTITLEMENT TO SMALL ENTITY STATUS

☒ Patentee is no longer entitled to small entity status. See 37 CFR 1.27(g)

## 3. MAINTENANCE FEE (37 CFR 1.20(e)-(g))

The appropriate maintenance fee must be submitted with this petition, unless it was paid earlier.

NOT Small Entity			Small Entity		
Amount	Fee	(Code)	Amount	Fee	(Code)
<input checked="" type="checkbox"/> \$ 980.00	3 ½ yr fee	(1551)	<input checked="" type="checkbox"/> \$ _____	3 ½ yr fee	(2551)
<input type="checkbox"/> \$ _____	7 ½ yr fee	(1552)	<input type="checkbox"/> \$ _____	7 ½ yr fee	(2552)
<input type="checkbox"/> \$ _____	11 ½ yr fee	(1553)	<input type="checkbox"/> \$ _____	11 ½ yr fee	(2553)

MAINTENANCE FEE BEING SUBMITTED \$ 980.00

## 4. SURCHARGE

The surcharge required by 37 CFR 1.20(i)(1) of \$ 700.00 (Fee Code 1557) must be paid as a condition of accepting unavoidably delayed payment of the maintenance fee.

SURCHARGE FEE BEING SUBMITTED \$ 700.00

## 5. MANNER OF PAYMENT

- ☐ Enclosed is a check for the sum of \$ \_\_\_\_\_
- ☒ Please charge Deposit Account No. 11-0600 the sum of \$ 1,680.00
- ☐ Payment by credit card. Form PTO-2038 is attached.

## 6. AUTHORIZATION TO CHARGE ANY FEE DEFICIENCY

- ☒ The Director is hereby authorized to charge any maintenance fee, surcharge or petition fee deficiency to Deposit Account No. 11-0600

[Page 2 of 4]

AUG 19 2010

PTO/SB/65 (03-09)

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U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

## 7. OVERPAYMENT

As to any overpayment made, please

☒ Credit to Deposit Account No. 11-0600

OR

☐ Send refund check

## WARNING:

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

## 8. SHOWING

The enclosed statement will show that the delay in timely payment of the maintenance fee was unavoidable since reasonable care was taken to ensure that the maintenance fee would be paid timely and that this petition is being filed promptly after the patentee was notified of, or otherwise became aware of, the expiration of the patent. The statement must enumerate the steps taken to ensure timely payment of the maintenance fee; the date and the manner in which the patentee became aware of the expiration of the patent, and the steps taken to file the petition promptly.

## 9. PETITIONER(S) REQUESTS THAT THE DELAYED PAYMENT OF THE MAINTENANCE FEE BE ACCEPTED AND THE PATENT REINSTATED.

/Alan P. Force/

August 19, 2010

Signature(s) of Petitioner(s)

Date

Alan P. Force

39,673

Typed or printed name(s)

Registration Number, if applicable

Kenyon &amp; Kenyon LLP

212-425-7200

Address

Telephone Number

One Broadway, New York, NY 10004

Address

## ENCLOSURES:

- ☒ Maintenance Fee Payment
- ☒ Statement why maintenance fee was not paid timely
- ☒ Surcharge under 37 CFR 1.20(i)(1) (fee for filing the maintenance fee petition)
- ☒ Other:

(1) Copy of U.S. Patent No. 6,749,702; and  
(2) Declaration of Daniel V. Haun in Support of Petition Under 37 CFR 1.378(B)  
(3) Notification of Loss of Entitlement to Small Entity Status

PTO/SB/85 (03-09)

Approved for use through 03/31/2012. OMB 0651-0016

U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

37 CFR 1.378(d) states: "Any petition under this section must be signed by an attorney or agent registered to practice before the Patent and Trademark Office, or by the patentee, the assignee, or other party in interest."

/Alan P. Force/

Signature

August 19, 2010

Date

Alan P. Force

Type or printed name

39,673

Registration Number, if applicable

**STATEMENT**

(In the space below, please provide the showing of unavoidable delay recited in paragraph 8 above.)

PLEASE SEE ATTACHED PAGES FOR SHOWING OF UNAVOIDABLE DELAY (3 PAGES ADDITIONAL)

(Please attach additional sheets if additional space is needed)

13332/16

U.S. PATENT NO. 6,749,702

## ADDITIONAL SHEETS TO PARAGRAPH 8: SHOWING OF UNAVOIDABLE DELAY

The delay in the payment of the Maintenance Fee for the above-identified patent was unavoidable, as reasonable care was taken to ensure that the maintenance fee was timely paid, and this petition is being filed promptly upon discovery by the Patentee of the expiration of the above-identified patent.

Based on my knowledge and belief, the facts that resulted in the unavoidably delayed payment of the maintenance fee are as follows:

I, Alan P. Force, the undersigned, received my Ph.D. in Physical Chemistry from Cornell University in 1981 and my J.D. from Fordham Law School in 1993. I have been a practicing patent attorney since 1994. On December 1, 2004, I began my tenure as an associate attorney in the New York office of Kenyon & Kenyon LLP (Kenyon). At my previous places of employment, I was responsible for the prosecution and maintenance of the patent applications and patents of Talley Defense Systems, Mesa, Arizona (TDS), now Nammo Talley, Inc.

Shortly thereafter, I informed Dr. Gregory Knowlton, the first named inventor, and now Chief Scientist at Nammo Talley, that I had changed my employment to Kenyon. Dr. Knowlton stated his desire to transfer responsibility for TDS patents to Kenyon. At Dr. Knowlton's request, I contacted Ms. Sue Kobyleski, Director of Materiel & Regulatory Affairs TDS. Ms. Kobyleski approved the transfer of responsibility. On or about March 8, 2004, Ms. Kobyleski forwarded an executed Engagement Letter between Kenyon and TDS to Kenyon.

Under my supervision, Kenyon staff prepared a separate Revocation/Power of Attorney for each of the 17 TDS patents. After execution by Mr. Haun, each of the separate Revocations/Powers of Attorney was filed by Kenyon. Each Revocation/Power of Attorney included a request for a change of correspondence address, and appointed the practitioners associated with Kenyon's customer number, 26646, to practice and transact all business in the U.S. P.T.O. connected to the patent identified on the particular Revocation/Power of Attorney. Each Revocation/Power of Attorney requested that all future correspondence from the U.S. P.T.O. be addressed to me at the New York Kenyon address provided in this document.

The Revocation/Power of Attorney for the above-identified patent was filed on July 31, 2006. The file history of the above-identified patent, obtained from the U.S. P.T.O., includes a copy of the filed Revocation/Power of Attorney with the request for the change in correspondence address. The Revocation/Power of Attorney in the file history is stamped as

Additional Page 1

received by the U.S. P.T.O. However, a recent check of the U.S. P.T.O. PAIR website indicates that the correspondence address for the above-identified patent remains that of the New York office of Fitzpatrick Cella Harper & Scinto (Fitzpatrick), my former employer, and lists the contact information for the attorneys of that firm.

The file history obtained from the U.S. P.T.O. does not include a Notice of Patent Expiration for the above-identified patent. Kenyon has no record of receiving a Notice of Patent Expiration for the above-identified patent, and has no record of receiving a Notice of Patent Expiration for the above-identified patent from Fitzpatrick if such a Notice was forwarded to the address of that firm.

In a letter dated January 18, 2006, Kenyon informed TDS that Kenyon would cease to be responsible for handling the monitoring and payment of maintenance fees for U.S. issued patents. The letter recommended that the Patentee engage Computer Patent Annuities Limited Partnership ("CPA") or a like service to handle the monitoring and payment of the maintenance fees for the TDS patents. Mr. Haun has confirmed that TDS followed Kenyon's recommendation. In a letter to TDS, CPA informed TDS that CPA would take over responsibility for the payment of maintenance fees on June 1, 2006.

On or about June 22, 2010, Kenyon received a Notice of Patent Expiration for U.S. Patent No. 5,739,460 (the '460 patent). As a result of the receipt of the Notice of Patent Expiration, Kenyon staff checked the status of all the TDS patents, and determined that eight of the patents assigned to TDS, including the above-identified patent, had expired as a result of the non-payment of a maintenance fee.

I conferred with Dr. Knowlton regarding the expiration of the patents, and was instructed to file the Petitions necessary to have the U.S. P.T.O. accept the delayed payment of the maintenance fees. Petitions to Accept Unintentionally Delayed Payment of Maintenance Fee in an Expired Patent under 37 C.F.R. 1.378 (c) were filed on July 29, 2010, for the four TDS patents that had been expired for less than two years.

I also discussed the steps that TDS had taken to insure the timely payment of the maintenance fees for the TDS patents with Dr. Knowlton and Mr. Haun. A Declaration of Mr. Haun detailing those steps is submitted herewith in support of this petition. At the time Mr. Haun signed his Declaration, Kenyon had only determined that six of the TDS patents had expired. It was later determined that two additional patents had expired. In that Declaration, Mr.

Additional Page 2

Haun confirms that he was not aware of any missed maintenance fee payments or the expiration of any of the Patentee's patents until the receipt of the June 29, 2010, Kenyon letter, forwarding the Notice of Patent Expiration for the '460 patent. In that Declaration, Mr. Haun further confirms that, prior to the June 29, 2010, Kenyon letter, he was not aware of any correspondence informing TDS that a maintenance fee was due for any of the expired TDS patents or that any of the TDS patents had expired.

As noted above, Mr. Haun was responsible for authorizing CPA to pay the maintenance fee. However, Mr. Haun was not aware the payment of the maintenance fee was delayed or that the above-identified patent had expired. Therefore, Mr. Haun was unable to authorize timely payment of the maintenance fee, and the delayed payment of the maintenance fee was unavoidable. It is respectfully submitted that this petition is being promptly filed after the Patentee became aware of the expiration of the patent.

In light of the above, the attorneys for the Patentee respectfully request acceptance of the unavoidably delayed maintenance fee and the reinstatement of U.S. Patent No. 6,749,702.

Additional Page 3

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13332/16

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Inventors : G. Knowlton et al.  
Patent No. : 6,749,702  
Issue Date : June 15, 2004  
For : LOW TEMPERATURE AUTOIGNITION COMPOSITION

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AUG 26 2010

OFFICE OF PETITIONS

Mail Stop PETITIONS  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**DECLARATION OF DANIEL V. HAUN IN SUPPORT OF  
PETITION UNDER 37 C.F.R. 1.378(B) TO ACCEPT UNAVOIDABLY DELAYED  
PAYMENT OF MAINTENANCE FEE IN EXPIRED PATENT**

I, Daniel V. Haun, declare the following:

I am VP Engineering and Research of Nammo Talley, Inc., formerly doing business as Talley Defense Systems, Inc., of Mesa, Arizona, ("the Patentee"). The Patentee is the assignee of the entire right and title of U.S. Patent No. 6,749,702, which issued June 15, 2004. It is my understanding that this Declaration is being submitted to the Commissioner of Patents with a Petition, requesting that the U.S. P.T.O. accept a delayed payment of the maintenance fee for the above-identified that was due on December 15, 2007.

The delay in the payment of the fee was unavoidable, as reasonable care was taken to ensure that the maintenance fee was timely paid, and this petition is being filed promptly upon notification of the Patentee of the expiration of the above-identified patent.

Based on my knowledge and belief, the facts that resulted in the unavoidably delayed payment of the maintenance fee are as follows:

In January 2006, the Patentee received a letter dated January 18, 2006, from Kenyon & Kenyon LLP ("Kenyon"), the Patentee's outside patent counsel, and attorneys of record for the above-identified patent. The January 18, 2006, letter informed the Patentee that Kenyon would cease handling the monitoring and payment of maintenance fees for U.S. issued patents. The letter recommended that the Patentee engage Computer Patent Annuities Limited Partnership

("CPA") to handle the monitoring and payment of the maintenance fees for the Patentee's patents. The Patentee followed Kenyon's recommendation.

In a letter to the Patentee, dated May 12, 2006, CPA confirmed that that organization would assume responsibility for the payment of the maintenance fees for the Patentee's patents. The May 12, 2006, letter stated that CPA would take over responsibility for the payment of maintenance fees on June 1, 2006, and that Patentee's next correspondence from CPA would be in the form of a renewal notice. According to the CPA letter, the renewal notice would be sent when the first maintenance fee for one of the Patentee's patents became due. It was my understanding that all correspondence from CPA would be directed to me.

The Patentee is not aware of the receipt of any further correspondence from CPA until an exchange of emails between Ms. Sallie Winkler, a Service Account Manager for CPA, and me on or about December 1, 2008. The purpose of the emails was to change the status of the Patentee from that of a small entity to that of a large entity. There was no indication in any of the emails I received from Ms. Winkler that a maintenance fee was due for any of the Patentee's patents or that any of those patents had expired as a result of the delayed payment of a maintenance fee.

The Patentee was not aware of any missed maintenance fee payments or the expiration of any of the Patentee's patents until the receipt of a letter from Kenyon, dated June 29, 2010. The June 29, 2010, Kenyon letter forwarded a Notice of Patent Expiration for the Patentee's U.S. Patent No. 5,739,460 to the Patentee that Kenyon had received from the U.S. P.T.O.

Kenyon further informed the Patentee that a check of the status of the Patentee's patents showed that six patents, including the above-identified patent, had expired between September 28, 2007, and April 14, 2010, as a result of the delayed payment of the required maintenance fees. Kenyon informed the Patentee that a Petition to Accept Unintentionally Delayed Payment of Maintenance Fee for each of the Patentee's patents that had been expired for less than two years would be filed as soon as possible, but that the revival of the above-identified patent would require a Petition to Accept Unavoidably Delayed Payment of Maintenance Fee with this statement. The Patentee immediately instructed Kenyon to prepare the required Petition, and do whatever was required to revive the Patentee's expired patents. Kenyon informed the Patentee that a Petition to Accept Unintentionally Delayed Payment of Maintenance Fee was submitted for each of the Patentee's patents that had been expired for less than two years on July 29, 2010.

I hereby declare that all statements made herein to my own knowledge are true and all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the Patentee's ability to enforce the above-identified patent.

Dated:

08/09/2010

By:



Daniel V. Haun  
VP Engineering and Research  
Nammo Talley, Inc.

Attorney Docket No. 13332/16

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE****RECEIVED  
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PATENTEE : GREGORY D. KNOWLTON  
SERIAL NO. : 09/010,822  
FILING DATE : January 28, 1998  
PATENT NO. : 6,749,702  
ISSUE DATE : June 15, 2004  
CONF. NO. : 9133  
FOR : LOW TEMPERATURE AUTOIGNITION COMPOSITION

**RECEIVED****AUG 26 2010****OFFICE OF PETITIONS**

Director of the United States Patent  
& Trademark Office  
Attn.: Maintenance Fee  
2051 Jamieson Avenue, Suite 300  
Alexandria, VA 22314

I hereby certify that this correspondence is being transmitted to the  
United States Patent & Trademark Office via facsimile (571-273-6500)  
on

Date: August 19, 2010

Signature: /Daniel G. Harris/  
Daniel G. Harris

**NOTIFICATION OF LOSS OF ENTITLEMENT TO SMALL ENTITY STATUS  
PURSUANT TO 37 C.F.R. § 1.27(g)(2)**

SIR:

Patentee hereby notifies the United States Patent and Trademark Office of loss of entitlement to small entity status. Patentee requests that the Office make large entity status of record in the application.

The Office is hereby authorized to charge any fees associated with the filing of this paper to Deposit Account No. 11-0600.

Respectfully submitted,

Date: August 19, 2010

By: /Alan P. Force/  
Alan P. Force (Reg. No. 39,673)  
KENYON & KENYON LLP  
One Broadway  
New York, N.Y. 10004  
Tel.: (212) 425-7200  
Fax.: (212) 425-5288  
CUSTOMER NO. 26646



US006749702B1

(12) **United States Patent**  
Knowlton et al.

(10) Patent No.: **US 6,749,702 B1**  
(45) Date of Patent: **\*Jun. 15, 2004**

(54) **LOW TEMPERATURE AUTOIGNITION COMPOSITION**

(75) Inventors: Gregory D. Knowlton, Chandler, AZ (US); Christopher P. Ludwig, Fountain Hills, AZ (US)

(73) Assignee: Talley Defense Systems, Inc., Mesa, AZ (US)

(\*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: 09/010,822

(22) Filed: Jan. 22, 1998

**Related U.S. Application Data**

(63) Continuation-in-part of application No. 08/645,945, filed on May 14, 1996, now Pat. No. 5,959,242.

(51) Int. Cl.<sup>7</sup> ..... C06B 33/08

(52) U.S. CL ..... 149/38; 149/37; 149/43; 149/45; 102/205

(58) Field of Search ..... 102/205; 149/37; 149/38; 43, 45, 41, 40

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\* cited by examiner

Primary Examiner—Aileen B. Felton

(74) Attorney, Agent, or Firm—Furpatrick, Cella, Harper & Scinto

(57) **ABSTRACT**

The present invention relates to a low temperature autoignition composition for safely initiating combustion of a main pyrotechnic charge in a gas generator or pyrotechnic device exposed to flame or a high temperature environment. The low temperature autoignition compositions of the invention include a mixture of an oxidizer and a powdered metal, wherein the oxidizer includes silver nitrate or a comelt or mixture comprising silver nitrate and at least one of an alkali metal nitrate, an alkaline earth metal nitrate, a complex salt nitrate, a dried, hydrated nitrate, an alkali metal chlorate, an alkali metal perchlorate, an alkaline earth metal chlorate, an alkaline earth metal perchlorate, ammonium perchlorate, sodium nitrite, potassium nitrite, silver nitrite, a complex salt nitrite, a solid organic nitrate, a solid organic nitrite, or a solid organic amine, and where the metal fuel and oxidizer are present in amounts sufficient to provide an autoignition composition having an autoignition temperature of no more than about 232° C. The present invention also relates to a method for initiating a gas generator or pyrotechnic composition in a gas generator or pyrotechnic device exposed to flame or a high temperature environment. In the method of the invention, the gas generator or pyrotechnic composition is placed in thermal contact with a low temperature autoignition composition of the invention.

31 Claims, No Drawings

US 6,749,702 B1

1

## LOW TEMPERATURE AUTOIGNITION COMPOSITION

This application is a continuation-in-part of U.S. application Ser. No. 08/645,945, filed on May 14, 1996 now U.S. Pat. No. 5,959,242.

### FIELD OF THE INVENTION

The invention relates to gas generating compositions, such as those used in "air bag" passive restraint systems, and, in particular, to autoignition compositions that provide a means for initiating combustion of a main pyrotechnic charge in a gas generator or pyrotechnic device exposed to temperatures significantly above the temperatures at which the unit is designed to operate.

### BACKGROUND OF THE INVENTION

One method commonly used for inflating air bags in vehicle passive restraint systems involves the use of an ignitable gas generator that generates an inflating gas by an exothermic reaction of the components of the gas generator composition. Because of the nature of passive restraint systems, the gas must be generated, and the air bag deployed in a matter of milliseconds. For example, under representative conditions, only about 60 milliseconds elapse between primary and secondary collisions in a motor vehicle accident, i.e., between the collision of the vehicle with another object and the collision of the driver or passenger with either the air bag or a portion of the vehicle interior.

In addition, the inflation gas must meet several stringent requirements. The gas must be non-toxic, non-noxious, must have a generation temperature that is low enough to avoid burning the passenger and the air bag, and it must be chemically inert so that it is not detrimental to the mechanical strength or integrity of the bag.

The stability and reliability of the gas generator composition over the life of the vehicle are also extremely important. The gas generator composition must be stable over a wide range of temperature and humidity conditions, and must be resistant to shock, so that it is virtually impossible for the gas generator to be set off except when the passive restraint system is activated by a collision.

Typically, the inflation gas is nitrogen, which is produced by the decomposition reaction of a gas generator composition containing a metal azide. One such gas generator composition is disclosed in Reissued U.S. Pat. No. Re. 32,584. The solid reactants of the composition include an alkali metal azide and a metal oxide, and are formulated to ignite at an ignition temperature of over about 315° C.

The gas generator composition is typically stored in a metal inflator unit mounted in the steering wheel or dashboard of the vehicle. Several representative inflator units are disclosed in U.S. Pat. Nos. 4,923,212, 4,907,819, and 4,865,635. The combustion of the gas generator composition in these devices is typically initiated by an electrically activated initiating squib, which contains a small charge of an electrically ignitable material, and is connected by electrical leads to at least one remote collision sensing device.

Due to the emphasis on weight reduction for improving fuel mileage in motorized vehicles, inflator units are often formed from light weight materials, such as aluminum, that can lose strength and mechanical integrity at temperatures significantly above the normal operating temperature of the unit. Although the temperature required for the unit to lose strength and mechanical integrity is much higher than will

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be encountered in normal vehicle use, these temperatures are readily reached in, for example, a vehicle fire. As the operating pressure of standard pyrotechnics increases with increasing temperature, a gas generator composition at its autoignition temperature will produce an operating pressure that is too high for a pressure vessel that was designed for minimum weight. Moreover, the melting point of many non-azide gas generator compositions is low enough for the gas generator composition to be molten at the autoignition temperature of the composition, which can result in a loss of ballistic control and excessive operating pressures. Therefore, in a vehicle fire, the ignition of the gas generator composition can result in an explosion in which fragments of the inflation unit are propelled at dangerous and potentially lethal velocities.

To prevent such explosions, air bags have typically included an autoignition composition that will autoignite and initiate the combustion of the main gas generating pyrotechnic charge at a temperature below that at which the shell or housing begins to soften and lose structural integrity. The number of autoignition compositions available in the prior art is limited, and includes nitrocellulose and mixtures of potassium chlorate and a sugar. However, nitrocellulose decomposes with age, so that the amount of energy released upon autoignition decreases, and may become insufficient to properly ignite the main gas generator charge. Moreover, prior art autoignition compositions have autoignition temperatures that are too high for some applications, e.g., non-azide auto air bag main charge generators.

Therefore, a need exists for a stable autoignition composition that is capable of igniting the gas generator composition at a temperature that is sufficiently low that the inflator unit maintains mechanical integrity at the autoignition temperature, but which is significantly higher than the temperatures reached under normal vehicle operating conditions.

### SUMMARY OF THE INVENTION

The present invention relates to an autoignition composition for safely initiating combustion in a main pyrotechnic charge in a gas generator or pyrotechnic device exposed to flame or a high temperature environment. The autoignition compositions of the invention comprise a mixture of an oxidizer and a powdered metal fuel, where the oxidizer comprises at least one of an alkali metal or an alkaline earth metal nitrate, a complex salt nitrate, such as  $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$  or  $\text{ZrO}(\text{NO}_3)_2$ , a dried, hydrated nitrate, such as  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  or  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ , silver nitrate, an alkali or alkaline earth metal chlorate or perchlorate, ammonium perchlorate, a nitrite of sodium, potassium, or silver, or a solid organic nitrate, nitrite, or amine, such as guanidine nitrate, nitroguanidine and 5-aminotetrazole, respectively. Preferably, the oxidizer comprises silver nitrate or a complex salt nitrate, a dried, hydrated nitrate, an alkali metal chlorate, an alkali metal perchlorate, an alkaline earth metal chlorate, an alkaline earth metal perchlorate, ammonium perchlorate, sodium nitrite, potassium nitrite, silver nitrite, a complex salt nitrite, a solid organic nitrate, a solid organic nitrite, or a solid organic amine, and the metal fuel and oxidizer are present in amounts sufficient to provide an autoignition composition having an autoignition temperature of no more than about 232° C.

Typically, the autoignition temperature, the temperature at which the autoignition compositions of the invention sponta-

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laneously ignite or autoignite, is between about 80° C. and about 232° C. To obtain the desired autoignition temperature, the autoignition compositions of the invention may further comprise an alkali or alkaline earth chloride, fluoride, or bromide comelted with a nitrate, nitrite, chlorate, or perchlorate, such that the autoignition composition has a eutectic or peritectic in the range of about 80° C. to about 250° C. In addition, for compositions with low output energy, an output augmenting composition, which comprises an energetic oxidizer of ammonium perchlorate or an alkali metal chlorate, perchlorate or nitrate, in combination with a metal, may be added to the composition.

Preferred autoignition compositions include oxidizers of a comelt of silver nitrate and alkali metal or alkaline metal nitrates, nitrites, chlorates or perchlorates, or a nitrite of sodium, potassium, or silver, and mixtures of silver nitrate and solid organic nitrates, nitrites, or amines.

The powdered metals useful as fuel in the present invention include molybdenum, magnesium, calcium, strontium, barium, titanium, zirconium, vanadium, niobium, tantalum, chromium, tungsten, manganese, iron, cobalt, nickel, copper, zinc, cadmium, tin, antimony, bismuth, aluminum, cerium, and silicon. It should be noted that molybdenum appears to be unique in its reactivity with the oxidizers described above, and is therefore the preferred metal fuel.

The most preferred inorganic autoignition compositions include comelts of silver nitrate and potassium nitrate, mixed with powdered molybdenum metal. In such an autoignition composition, the comelt is ground to a particle size of about 10 to about 30 microns, and the molybdenum powder has a particle size of less than about 2 microns. The mole fraction of silver nitrate in the comelt is typically about 0.4 to about 0.6, the mole fraction of potassium nitrate in the comelt is about 0.6 to 0.4, and the comelt is mixed with at least a stoichiometric amount of molybdenum powder.

The most preferred organic autoignition compositions include a mixture of silver nitrate, guanidine nitrate, and molybdenum. In such an autoignition composition, the amount of molybdenum may be varied to adjust the autoignition temperature. If the amount of molybdenum is greater than the stoichiometric amount, the autoignition temperature of the autoignition composition will decrease as the amount of molybdenum is increased.

The present invention also relates to a method for safely initiating combustion of a gas generator or pyrotechnic composition in a gas generator or pyrotechnic device having a housing when the gas generator or pyrotechnic device is exposed to flame or a high temperature environment. The method of the invention comprises forming an autoignition composition, as described above, and placing the autoignition composition in thermal contact with the gas generator or pyrotechnic composition within the gas generator or pyrotechnic device, such that the autoignition composition autoignites and initiates combustion of the gas generator or pyrotechnic composition when the gas generator or pyrotechnic device is exposed to flame or a high temperature environment. The method of the invention may also include the step of mixing the autoignition composition with an output augmenting composition, as described above, such that the autoignition composition autoignites and initiates combustion of the output augmenting composition, which, in turn, initiates combustion of the gas generator or pyrotechnic composition when the gas generator or pyrotechnic device is exposed to flame or a high temperature environment.

#### DETAILED DESCRIPTION OF THE INVENTION

The autoignition compositions of the invention are suitable for use with a variety of gas generating and pyrotechnic

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devices, in particular, vehicle restraint system air bag inflators. The autoignition compositions ensure that the gas generating or pyrotechnic device functions properly and safely when exposed to a high temperature environment, i.e., that combustion of the main pyrotechnic charge is initiated at a temperature below the temperature at which the material used to form the shell or housing begins to weaken or soften. If the autoignition composition is not utilized, the device may not function properly or safely if exposed to high heat or flame, because the operating pressure of standard pyrotechnics increases with increasing temperature. Therefore, a gas generator composition at its autoignition temperature can produce an operating pressure that is too high for a pressure vessel that was designed for minimum weight. Moreover, the melting point of many non-azide gas generator compositions is low enough for the gas generator composition to be molten at the autoignition temperature of the composition, which can result in a loss of ballistic control and excessive operating pressures. As a result, under high temperature conditions the components of the gas generator or pyrotechnic composition within the device can decompose, melt, or sublime, and burn at an accelerated rate, resulting in an explosion that would destroy the device, and could possibly propel harmful or lethal fragments. The autoignition compositions of the invention provide an effective means for preventing such a catastrophic occurrence.

The pyrotechnic autoignition compositions of the invention provide several advantages over typical autoignition materials currently in use, such as microcellulose, including a lower autoignition temperature and better thermal stability. The preferred compositions autoignite over a narrow temperature range, and provide extremely repeatable performance. The complete series of compositions described and claimed herein have a wide range of autoignition temperatures that can be tailored for particular applications. The autoignition compositions also may have low to moderate hazard sensitivities, i.e., DOT 1.3c or lower.

The autoignition compositions of the invention comprise a mixture of a powdered metal fuel and an oxidizer of one or more alkali metal or alkaline earth metal nitrates, silver nitrate, alkali or alkaline earth metal chlorates or perchlorates, ammonium perchlorate, nitrites of sodium, potassium, or silver, or a complex salt nitrate, such as ceric ammonium nitrate,  $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ , or zirconium oxide dinitrate,  $\text{ZrO}(\text{NO}_3)_2$ . As used herein, the term "powdered metal" encompasses metal powders, particles, prills, flakes, and any other form of the metal that is of the appropriate size and/or surface area for use in the present invention, i.e., typically, with a dimension of less than about 100 microns. When more than one oxidizer is used in the composition, they may be provided either as a mixture or a comelt. Comelts have eutectics and/or peritectics in the range of about 80° to 250° C.

Solid organic nitrates,  $\text{R}-(\text{ONO}_2)_n$ , nitrites,  $\text{R}-(\text{NO}_2)_n$ , and amines  $\text{R}-(\text{NH}_2)_n$ , can also be used as the oxidizer component, either alone or in combination with one or more other solid organic nitrate, nitrite, or amine, or with one or more of the inorganic nitrates, nitrites, chlorates or perchlorates listed above, but preferably only as mechanical mixes because in some cases comelts of these solid organic materials with inorganic/organic oxidizers may produce unstable combinations. Preferably the solid organic nitrates, nitrites and amines that are useful in forming the autoignition compositions of the invention have melting points between about 80° C. and about 250° C. When heated, mixtures should preferably produce eutectics and peritectics in the range of about 80° C. to about 250° C. These mixtures may

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be combined with one or more of the metals disclosed herein, and can be used in a powdered, granular or pelletized form.

It has also been determined using selected hydrated metal nitrates, such as  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$ , that hygroscopic, low melting point metal nitrates can be dehydrated and stabilized relative to moisture absorption by comelting with anhydrous metal nitrates, such as those described above. It is believed that many other low melting point, hydrated metal nitrates of the general formula  $\text{M}(\text{NO}_3)_x \cdot \text{YH}_2\text{O}$ , including, but not limited to, the nitrates of chromium, manganese, cobalt, iron, nickel, zinc, cadmium, aluminum, bismuth, cerium and magnesium, can also be dehydrated and stabilized relative to moisture absorption and rehydration by comelting with anhydrous metal nitrates, nitrites, chlorates and/or perchlorates. These comelts can be combined with metals to produce low temperature (80° C. to 250° C.) autoignition compositions.

The output energy of certain autoignition compositions taught herein, in particular, certain nitrate/nitrite/metal systems, is very low, and may not be sufficient to ignite the ignition enhancer or ignition booster charge. Autoignition compositions of this type may require an output augmenting material or charge to initiate combustion of the enhancer and main pyrotechnic charge. The ignition train for such a composition is initiated when the autoignition composition is heated to the autoignition temperature and ignites. The heat generated by the combustion of the autoignition device ignites the output augmenting material, which, in turn, ignites the enhancer and main pyrotechnic charge of the gas generator. The augmentation material can be a charge which is separate from the autoignition material, or is mixed in with the autoignition composition to boost its output. Typically, an output augmenting composition comprises an energetic oxidizer, such as ammonium perchlorate or alkali metal chlorate, perchlorate or nitrate, and a metal such as Mg, Ti, or Zr or a nonmetal such as boron.

In addition, the presence of certain metal oxides in a nitrate, nitrite, chlorate or perchlorate oxidizer mix or comelt of the invention can have a catalytic effect in lowering the autoignition temperature for the reaction of the oxidizer and the metal, which is equivalent to lowering the energy of activation. Metal oxides useful in the invention for this purpose include, but are not limited to  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Cr}_2\text{O}_3$ , and transition metal oxides, which include, but are not limited to  $\text{V}_2\text{O}_5$ ,  $\text{CrO}_2$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Co}_2\text{O}_3$ ,  $\text{NiO}$ ,  $\text{CuO}$ ,  $\text{ZnO}$ ,  $\text{ZrO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{MoO}_3$ , and  $\text{Ag}_2\text{O}$ .

In the autoignition compositions of the invention, the nitrate, nitrite, chlorate or perchlorate component or components function as an oxidizer, and the metal serves as a fuel. For example, the reaction of a composition comprising a comelt of metal nitrates and a metal proceeds according to the general equation

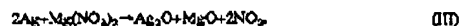


The driving force for this reaction appears to follow the activity series or electromotive series for metals, in which metallic elements higher in the series will displace, i.e., reduce, elements lower in the series from a solution or melt. In particular, oxidizer systems containing silver nitrate and/or silver nitrite will generally yield very efficient autoignition materials with respect to ease, rate, and intensity of reaction when compounded with metals which are high in the activity or electromotive series. For example, Mg, Al, Mn, Zn, Cr, Fe, Cd, Co, Ni and Mo are all well above Ag in the series. A typical reaction is represented by equations II to V.



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In this high temperature, molten salt environment neither the  $\text{Mg}(\text{NO}_3)_2$  nor the Ag metal are stable, and a second reaction quickly occurs to produce metal and nitrogen oxides:



When potassium nitrate is also present in the comelt, the following reaction also occurs.



Summing equations II, III, and IV, yields a net reaction that was given in general terms as equation I. For a composition of silver nitrate, potassium nitrate and magnesium, the net reaction is:



A comparison of Differential Scanning Calorimeter (DSC) and Calibrated Tube Furnace autoignition test results for inorganic, organic and mixed inorganic/organic nitrate, nitrite, chlorate and perchlorate oxidizer systems with selected metals, demonstrates that at least two different autoignition mechanisms may be involved. As described above, purely inorganic systems, e.g.,  $\text{KNO}_3/\text{AgNO}_3/\text{Mo}$ , generally autoignite in the vicinity of a thermal event clearly visible on a DSC scan, such as a crystalline phase transition, a melting point, or a eutectic or peritectic point. In some of the organic and mixed inorganic/organic systems it appears that autoignition of larger mass samples in the tube furnace can occur at much lower temperature than autoignition in the DSC without the presence of some small, lower temperature thermal event observed on the DSC. For example, the  $\text{CH}_3\text{N}_4\text{O}_3/\text{AgNO}_3/\text{Mo}$  system autoignites at 170-174° C. by DSC analysis with no visible thermal events prior to autoignition. However, a 200 mg sample of the same composition autoignites in the tube furnace at 138-158° C., depending on percent composition. It is possible that this is more than just a mass effect, and the dramatic reduction in autoignition temperatures observed in tube furnace testing, as compared to the results obtained with DSC testing, is possibly the result of some catalytic, self heating, or other thermal effect.

The amount of the nitrate, nitrite, chlorate or perchlorate used in an autoignition composition can vary significantly. For purely inorganic systems, the mole percent or molar ratio of the nitrate, nitrite, chlorate or perchlorate oxidizer components in binary and ternary mixes and comelts should be stoichiometrically balanced with the metal or metals in the final autoignition composition, i.e., the molar amounts of the oxidizer and metal fuel are substantially proportional to the molar amounts given in the balanced chemical equation for the reaction of the oxidizer with the fuel. However, it appears that the autoignition temperature for organic/inorganic compositions comprising molybdenum metal can be tailored by adjusting the molybdenum metal content from stoichiometrically balanced to extremely metal (fuel) rich. As the molybdenum metal content is increased the autoignition temperature decreases. It is believed that this holds true for the other metal fuels described above.

The amount of each oxidizer component in a mixture or comelt depends on the molar amounts of the oxidizers at or near the eutectic point for the specific oxidizer mixture or comelt composition. As a result the nitrate, nitrite, chlorate or perchlorate oxidizer component or components will be the major component in some autoignition compositions of the invention, and the powdered metal fuel will be the major component in others. Those skilled in the art will be able to determine the required amount of each component from the

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stoichiometry of the autoignition reaction or by routine experimentation.

The preferred compositions comprise a comelt of silver nitrate,  $\text{AgNO}_3$ , and a nitrate of an alkali metal or an alkaline earth metal, preferably, lithium nitrate,  $\text{LiNO}_3$ , sodium nitrate,  $\text{NaNO}_3$ , potassium nitrate,  $\text{KNO}_3$ , rubidium nitrate,  $\text{RbNO}_3$ , cesium nitrate,  $\text{CsNO}_3$ , magnesium nitrate,  $\text{Mg(NO}_3)_2$ , calcium nitrate,  $\text{Ca(NO}_3)_2$ , strontium nitrate,  $\text{Sr(NO}_3)_2$ , or barium nitrate,  $\text{Ba(NO}_3)_2$ , a nitrite of sodium,  $\text{NaNO}_2$ , potassium,  $\text{KNO}_2$ , and silver,  $\text{AgNO}_2$ , a chlorate of an alkali metal or an alkaline earth metal, preferably lithium chlorate,  $\text{LiClO}_3$ , sodium chlorate,  $\text{NaClO}_3$ , potassium chlorate,  $\text{KClO}_3$ , rubidium chlorate,  $\text{RbClO}_3$ , calcium chlorate,  $\text{Ca(ClO}_3)_2$ , strontium chlorate,  $\text{Sr(ClO}_3)_2$ , or barium chlorate,  $\text{Ba(ClO}_3)_2$ , or a perchlorate of an alkali metal or an alkaline earth metal, preferably lithium perchlorate,  $\text{LiClO}_4$ , sodium perchlorate,  $\text{NaClO}_4$ , potassium perchlorate,  $\text{KClO}_4$ , rubidium perchlorate,  $\text{RbClO}_4$ , cesium perchlorate,  $\text{CsClO}_4$ , magnesium perchlorate,  $\text{Mg(ClO}_4)_2$ , calcium perchlorate,  $\text{Ca(ClO}_4)_2$ , strontium perchlorate,  $\text{Sr(ClO}_4)_2$ , or barium perchlorate,  $\text{Ba(ClO}_4)_2$ . Preferred compositions also include mixtures of  $\text{AgNO}_3$  and the solid organic nitrate guanidine nitrate,  $\text{CH}_5\text{N}_3\text{O}_5$ .

The preferred metal fuels are molybdenum, Mo, magnesium, Mg, calcium, Ca, strontium, Sr, barium, Ba, titanium, Ti, zirconium, Zr, vanadium, V, niobium, Nb, tantalum, Ta, chromium, Cr, tungsten, W, manganese, Mn, iron, Fe, cobalt, Co, nickel, Ni, copper, Cu, zinc, Zn, cadmium, Cd, tin, Sn, antimony, Sb, bismuth, Bi, aluminum, Al, cerium, Ce, and silicon, Si. These metals may be used alone or in combination.

The most preferred metal fuel, molybdenum, appears to be unique in its reactivity with nitrate, nitrite, chlorate and perchlorate salts, mixes and comelts. Molybdenum metal has reacted and autoignited with every oxidizer and oxidizer system of nitrates, nitrites, chlorates and perchlorates tested. Although the mechanism is not fully understood, there appears to be a sensitizing or catalytic interaction between molybdenum and nitrates, nitrites, chlorates and perchlorates.

The binary and ternary oxidizer systems can be mixed by physical or mechanical means, or can be comelted to produce a higher level of ingredient intimacy in the mix. Repetitive comelting, preferably 2 to about 4 times, produces the highest level of ingredient intimacy and mix homogeneity. The oxidizers in mechanical mixes should each be ground to an average particle size (APS) of about 100 microns or less prior to mixing, preferably about 5 to about 20 microns. Comelts of oxidizers should also be ground to less than about 100 microns APS, again, with a preferred APS of about 5 to about 20 microns. Average particle size of the metals used in the autoignition compositions should be about 35 microns or less with the preferred APS being less than about 10 microns. The reaction or burning rate and ease of autoignition increases as mix intimacy and homogeneity increases, and as the average particle size of the oxidizers and metals decreases. In other words, reaction rate and ease of autoignition are proportional to mix intimacy and homogeneity and inversely proportional to the average particle size of the oxidizer and metal components.

The most preferred purely inorganic composition is a comelt of silver nitrate and potassium nitrate, ground to a particle size of about 20 microns, mixed with powdered molybdenum having a particle size of less than about 2 microns. The mole fraction of silver nitrate in the comelt is from about 0.4 to about 0.6, and the mole fraction of

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potassium nitrate is from about 0.6 to about 0.4. The composition further comprises an essentially stoichiometric amount of molybdenum.

The autoignition temperature can be adjusted and tailored for specific uses by varying the amounts and types of the metal nitrates in the comelt and the specific metal used. The most preferred compositions of  $\text{AgNO}_3/\text{KNO}_3/\text{Mo}$  have an autoignition temperature between 130° and 135° C.

For the majority of the compositions described herein, autoignition appears to occur very near a phase change. For example, a melting or crystal structure rearrangement of one of the oxidizers in a mechanical mix, or of the single oxidizer in simpler systems. In binary and ternary comelt systems, autoignition occurs near a eutectic or peritectic point. In all of the cases described above, the oxidizer softens or melts producing a kinetically favorable environment for reaction with the metal.

Each system of comelted oxidizers is unique. A simple binary system can have a single eutectic point, as described by the phase diagram of the system, that results in a single autoignition temperature for a specific metal/comelt composition. For example, a binary comelt of  $\text{LiNO}_3/\text{KNO}_3$  with molybdenum will autoignite at 230° C.

Other more complicated binary and ternary comelts can have eutectic and peritectic points that result in several different autoignition temperatures for a specific metal/comelt system. The autoignition temperature of the composition is dependent on the molar ratio of the oxidizers in the comelt. For example, a binary comelt of  $\text{AgNO}_3/\text{KNO}_3$  with molybdenum has an autoignition temperature near the peritectic point of 135° C. for comelts with less than 58 mole percent  $\text{AgNO}_3$ , based on the weight of the comelt, but has an autoignition temperature near the eutectic point of 118° C. for comelts with 58 mole percent  $\text{AgNO}_3$  or higher.

The eutectic and peritectic melting points of a binary system tends to set the upper limit for any ternary system containing the specific binary combination of oxidizers. In other words, the melting point or eutectic of a ternary system cannot be higher than the lowest melting point of a binary combination within it.

In some cases certain non-energetic salts such as alkali and alkaline earth chlorides, fluorides and bromides can be comelted with selected nitrates, nitrites, chlorates and perchlorates, preferably  $\text{AgNO}_3$  and  $\text{AgNO}_2$ , to produce eutectics or peritectics preferably in the range of about 80° C. to about 250° C. These comelts will be combined with any one or more of the listed metals to produce the autoignition reaction. Selected nitrates, chlorates, or perchlorates may also be added to augment ignition and output.

The autoignition composition of the invention is preferably placed within a gas generating or pyrotechnic device, e.g., within an inflator housing, where, when the inflator is exposed to flame or a high temperature environment, they operate in a manner that allows the autoignition composition to ignite and initiate combustion of the pyrotechnic charge of the device at a device temperature that is lower than the temperature at which the device loses mechanical integrity. As the operating pressure of standard pyrotechnics increases with increasing temperature, a gas generator composition at its autoignition temperature will produce an operating pressure that is too high for a pressure vessel that was designed for minimum weight. Moreover, the melting point of many non-azide gas generator compositions is low enough for the gas generator composition to be molten at the autoignition temperature of the composition, which can result in a loss of ballistic control and excessive operating pressures. Therefore, in a vehicle fire, the ignition of the gas generator

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composition can result in an explosion in which fragments of the inflation unit are propelled at dangerous and potentially lethal velocities. With the autoignition compositions of the present invention, the combustion of the main pyrotechnic charge is initiated at a temperature below the temperature at which the material used to form the shell or housing begins to weaken or soften, and the uncontrolled combustion of the gas generator or pyrotechnic composition at higher temperatures is prevented, which could otherwise result in an explosion of the device. Preferred locations within the gas generating or pyrotechnic device include a cup or recessed area at the bottom of the housing of the device, a coating or pellet affixed to the inner surface of the housing, or inclusion as part of the squib used to ignite the gas generator or pyrotechnic composition during normal operation.

The foregoing features, aspects and advantages of the present invention will become more apparent from the following non-limiting examples of the present invention.

## EXAMPLES

The determination of temperatures of autoignition, thermal decomposition, melting, eutectics and peritectics, crystalline rearrangements, etc. was performed on a Perkin-Elmer DSC-7 differential scanning calorimeter. Scanning rates ranged from 0.1° C./min to 100° C./min. Due to heat transfer effects at higher scan rates, the most accurate results were obtained at the slower scan rates (0.1 to 1.0° C./min). It should be noted, however, that the faster scan rates (50 to 100° C./min) are more representative of bonfire type heating.

A number of the autoignition compositions display mass effects that can affect the autoignition temperature. For example, a 6 mg sample of  $\text{LiClO}_4/\text{Mo}$  will autoignite at 146° C. on the DSC (1° C./min scan rate). This autoignition occurs just after a crystalline phase transition. On the other hand, a 2 mg sample does not autoignite until 237° C., which is just before the melting point of  $\text{LiClO}_4$  (248° C.). To address these mass effects on a larger scale and also to test application size samples, typically about 50 to about 250 grams, a tightly temperature controlled tube furnace is used. This also provides a practical means of determining time to autoignition at a selected temperature for various sample sizes ranging from about 50 to about 250 grams.

## Example 1

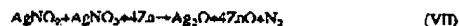


An autoignition composition was prepared by mixing a comelt of equimolar amounts of silver nitrate ( $\text{AgNO}_3$ ) and potassium nitrate ( $\text{KNO}_3$ ) with a stoichiometric amount of a molybdenum (Mo) metal according to equation VI, i.e., 39.4% by weight  $\text{AgNO}_3$ , 23.5% by weight  $\text{KNO}_3$ , and 37.1% by weight Mo. An autoignition temperature of 135±1° C. was determined for the composition using differential scanning calorimetry (DSC) with 2 to 8 mg samples. However, when a 200 mg sample was tested in a tube furnace, the autoignition temperature was 130±2° C., demonstrating the existence of a mass effect.

There are two melting points and, therefore, two autoignition temperatures associated with this set of materials. A composition with a weight percent of  $\text{AgNO}_3$  greater than 44.6% of the autoignition composition melts and autoignites at the eutectic at 118±2° C. However, with a weight percent of  $\text{AgNO}_3$  of less than 44.6%, the composition melts and autoignites at the peritectic at 135±2° C.

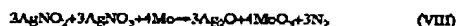
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## Example 2



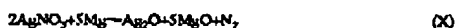
A comelt of equimolar amounts of silver nitrite,  $\text{AgNO}_2$ , and silver nitrate,  $\text{AgNO}_3$ , was mixed with a stoichiometric amount of zinc, Zn, metal in accordance with equation VII, i.e., 26.3% by weight  $\text{AgNO}_2$ , 29.0% by weight  $\text{AgNO}_3$ , and 44.7% Zn. An autoignition temperature of 130±2° C. was determined for the composition using DSC.

## Example 3



A comelt of equimolar amounts of  $\text{AgNO}_3$  and  $\text{AgNO}_2$  was mixed with a stoichiometric amount of Mo metal in accordance with equation VIII, i.e., 34.1% by weight  $\text{AgNO}_2$ , 37.6% by weight  $\text{AgNO}_3$ , and 28.3% by weight Mo. An autoignition temperature of 131±2° C. was determined for the composition using DSC.

## Example 5



$\text{AgNO}_3$  was mixed with a stoichiometric amount of magnesium, Mg, metal in accordance with equation X, i.e., 73.7% by weight  $\text{AgNO}_3$  and 26.3% by weight Mg. An autoignition temperature of 157±2° C. was determined for the composition using DSC.

## Example 6



$\text{AgNO}_3$  was mixed with a stoichiometric amount of potassium perchlorate,  $\text{KClO}_4$ , and Mg in accordance with equation XI, i.e., 19.9% by weight  $\text{KClO}_4$ , 48.7% by weight  $\text{AgNO}_3$ , and 31.4% by weight Mg. An autoignition temperature of 154±2° C. was determined for the composition using DSC.

It may be noted that the composition of example 5,  $\text{AgNO}_3/\text{Mg}$ , has about the same autoignition temperature, 157° vs 154° C., as the composition of example 6,  $\text{AgNO}_3/\text{KClO}_4/\text{Mg}$ . Accordingly, it might be concluded that the  $\text{AgNO}_3/\text{Mg}$  reaction is the driving force in both cases. However, the  $\text{AgNO}_3/\text{KClO}_4/\text{Mg}$  composition reacts with much greater energy than the  $\text{AgNO}_3/\text{Mg}$  composition. In general, perchlorates produce greater energy than nitrates in this type of reaction, and, thus, this example demonstrates output augmentation by  $\text{KClO}_4$ .

## Example 7



A comelt of equimolar amounts of lithium nitrate,  $\text{LiNO}_3$ , and  $\text{AgNO}_3$  was mixed with a stoichiometric amount of Mo metal, in accordance with equation XII, i.e., 17.3% by weight  $\text{LiNO}_3$ , 42.6% by weight  $\text{AgNO}_3$ , and 40.1% by weight Mo. An autoignition temperature of 175±2° C. was determined for the composition using DSC.

## Example 8



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A comelt of equimolar amounts of calcium nitrate,  $\text{Ca}(\text{NO}_3)_2$ , and  $\text{AgNO}_3$  was mixed with a stoichiometric amount of Mo metal, in accordance with equation XIII, i.e., 28.6% by weight  $\text{Ca}(\text{NO}_3)_2$ , 29.6% by weight  $\text{AgNO}_3$  and 41.8% by weight Mo. An autoignition temperature of  $193 \pm 2^\circ \text{C}$ . was determined for the composition using DSC.

The  $\text{Ca}(\text{NO}_3)_2$  was received as  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and was dried to remove the  $\text{H}_2\text{O}$  before comelting.

## Example 9



$\text{AgNO}_3$  was mixed with a stoichiometric amount of Mo in accordance with equation XIV, i.e., 68.0% by weight  $\text{AgNO}_3$  and 32.0% by weight Mo. This composition autoignited at  $199 \pm 2^\circ \text{C}$ . by DSC analysis.

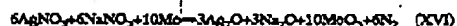
## Example 10



$\text{AgNO}_3$  was mixed with a stoichiometric amount of  $\text{KClO}_4$  and Mo in accordance with equation XV, i.e., 18.1% by weight  $\text{KClO}_4$ , 44.3% by weight  $\text{AgNO}_3$  and 37.6% by weight Mo. The composition autoignited at  $192 \pm 2^\circ \text{C}$ . as determined by DSC analysis.

As with the  $\text{AgNO}_3/\text{Mo}$  and  $\text{KClO}_4/\text{AgNO}_3/\text{Mo}$ , described above,  $\text{AgNO}_3/\text{Mo}$  autoignites at nearly the same temperature,  $199^\circ \text{C}$ . vs  $192^\circ \text{C}$ ., as the  $\text{KClO}_4/\text{AgNO}_3/\text{Mo}$ . However, the  $\text{KClO}_4/\text{AgNO}_3/\text{Mo}$  system autoignites with greater energy than the  $\text{AgNO}_3/\text{Mo}$ , and is another example of output augmentation by  $\text{KClO}_4$ .

## Example 11



A comelt of an equimolar ratio of  $\text{AgNO}_3$  and sodium nitrate,  $\text{NaNO}_3$ , was mixed with a stoichiometric amount of Mo metal in accordance with equation XVI, i.e., 20.5% by weight  $\text{NaNO}_3$ , 41.0% by weight  $\text{AgNO}_3$  and 38.5% by weight Mo. The composition autoignited at  $217 \pm 2^\circ \text{C}$ . by DSC analysis.

## Example 13



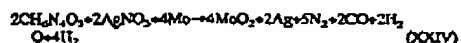
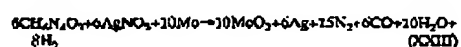
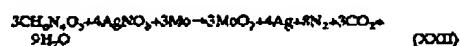
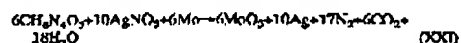
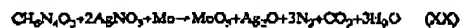
A 1:2 ratio of guanidine nitrate to  $\text{AgNO}_3$  was mixed with a stoichiometric amount of Mo in accordance with equation XIX, i.e., 21.9% by weight  $\text{CH}_6\text{N}_4\text{O}_3$ , 60.9%  $\text{AgNO}_3$  and 17.2% by weight Mo. The composition autoignited at  $172 \pm 2^\circ \text{C}$ . (by DSC).

This composition is also an example of organic nitrates in autoignition reactions. However, this composition is fully oxidized, and, therefore, requires no external source of oxygen.

Mass effects have been observed with this composition. For 2 to 8 mg samples, DSC autoignition temperatures between  $170$  and  $174^\circ \text{C}$ . were observed. Mass, thermal and possibly self-heating/catalytic effects become evident when

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larger samples, i.e., 50 to 250 mg, are heated in a tightly temperature controlled tube furnace. Autoignition temperatures ranging from  $128$  to  $158^\circ \text{C}$ . have been produced in the tube furnace with 200 mg samples of various  $\text{CH}_6\text{N}_4\text{O}_3/\text{AgNO}_3/\text{Mo}$  compositions in both powder and pellet form. The autoignition temperature for  $\text{CH}_6\text{N}_4\text{O}_3/\text{AgNO}_3/\text{Mo}$  compositions can be tailored by adjusting the molybdenum metal content from stoichiometrically balanced to extremely fuel (metal) rich. As the molybdenum metal content is increased the autoignition temperature decreases. The following balanced equations represent a progression from a fully oxidized  $\text{CH}_6\text{N}_4\text{O}_3/\text{AgNO}_3/\text{Mo}$  system through increasingly under oxidized or fuel rich systems.



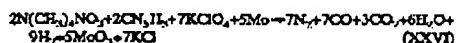
Amounts of molybdenum metal added in excess of the stoichiometric amount given in equation XX will produce thermal and possibly catalytic effects which further reduce the autoignition temperature.

## Example 14



Tetramethyl ammonium nitrate,  $\text{N}(\text{CH}_3)_4\text{NO}_3$ , was mixed with 5-aminotetrazole,  $\text{CN}_2\text{H}_3$ , potassium chlorate,  $\text{KClO}_4$ , and molybdenum, Mo, in accordance with equation XXV, i.e., 11.8% by weight  $\text{N}(\text{CH}_3)_4\text{NO}_3$ , 8.2% by weight  $\text{CN}_2\text{H}_3$ , 56.7% by weight  $\text{KClO}_4$  and 23.3% by weight Mo. An autoignition temperature of  $155 \pm 2^\circ \text{C}$ . was determined for this composition using DSC analysis. The 5-aminotetrazole used should be anhydrous.

## Example 15



Tetramethyl ammonium nitrate,  $\text{N}(\text{CH}_3)_4\text{NO}_3$ , was mixed with 5-aminotetrazole,  $\text{CN}_2\text{H}_3$ , potassium perchlorate,  $\text{KClO}_4$ , and molybdenum, Mo, in accordance with equation XXVI, i.e., 13.1% by weight  $\text{N}(\text{CH}_3)_4\text{NO}_3$ , 9.1% by weight  $\text{CN}_2\text{H}_3$ , 52.1% by weight  $\text{KClO}_4$  and 25.7% by weight Mo. An autoignition temperature of  $170 \pm 3^\circ \text{C}$ . was determined for this composition by DSC analysis. The 5-aminotetrazole used should be anhydrous.

The invention has also been successfully tested in timed autoignition tests at various temperatures, and in bench tests in prototype automobile air bag inflators.

While it is apparent that the disclosed invention is well calculated to fulfill the objectives stated above, it will be appreciated that numerous modifications and embodiments may be devised by those skilled in the art, and it is intended that the appended claims cover all such modifications and embodiments that fall within the true spirit and scope of the present invention.

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We claim:

1. A low temperature autoignition composition for safely initiating combustion of a main pyrotechnic charge in a gas generator or pyrotechnic device exposed to flame or a high temperature environment, consisting essentially of:

a mixture of a silver nitrate oxidizer composition and a powdered metal fuel, the silver nitrate oxidizer composition consisting essentially of one of:

(a) silver nitrate; or

(b) a comelt or mixture consisting essentially of silver nitrate and at least one additional component selected from the group consisting of an alkali metal nitrate, an alkaline earth metal nitrate, a complex salt nitrate, a dried hydrated nitrate, an alkali metal chlorate, an alkali metal perchlorate, an alkaline earth metal chlorate, an alkaline earth metal perchlorate, ammonium perchlorate, sodium nitrite, potassium nitrite, silver nitrite, a complex salt nitrite, a solid organic nitrate, and a solid organic nitrite;

wherein

the powdered metal fuel is selected from the group consisting of molybdenum, calcium, strontium, barium, titanium, zirconium, vanadium, niobium, tantalum, chromium, tungsten, manganese, iron, cobalt, nickel, copper, zinc, cadmium, tin, antimony, bismuth, aluminum, silicon, and mixtures thereof;

the silver nitrate oxidizer composition has at least one of a crystalline phase transition, a melting point, a eutectic point, or a peritectic point at a temperature of no more than about 250° C.;

the metal fuel is present in an amount at least substantially stoichiometric relative to the silver nitrate oxidizer composition; and

the mixture of metal fuel and silver nitrate oxidizer composition has a mix intimacy and homogeneity sufficient between the silver nitrate oxidizer composition and the metal fuel to react in an autoignition reaction of metal fuel and silver nitrate oxidizer composition at an autoignition temperature of no more than about 232° C., thereby providing an autoignition composition having the autoignition temperature of no more than about 232° C.; wherein heating the autoignition composition to the autoignition temperature results in a reaction between the silver nitrate and the metal fuel, thereby initiating the autoignition reaction.

2. The low temperature autoignition composition of claim 1, wherein the silver nitrate oxidizer composition is a comelt consisting essentially of silver nitrate and at least one of an alkali metal nitrate, alkali metal nitrite, alkali metal chlorate, alkali metal perchlorate, alkaline metal nitrate, alkaline metal nitrite, alkaline metal chlorate, alkaline metal perchlorate, sodium nitrite, potassium nitrite, or silver nitrite.

3. The low temperature autoignition composition of claim 2, wherein the powdered metal fuel is selected from the group consisting of molybdenum, titanium, zirconium, niobium, nickel, chromium, zinc, aluminum, and cerium.

4. The low temperature autoignition composition of claim 3, wherein the powdered metal fuel is selected from the group consisting of molybdenum, titanium, zirconium, zinc, and cerium.

5. The low temperature autoignition composition of claim 4, wherein the powdered metal fuel is molybdenum.

6. The low temperature autoignition composition of claim 4, wherein the silver nitrate oxidizer composition is selected from the group consisting of silver nitrate and comelts

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consisting essentially of silver nitrate and potassium nitrate, silver nitrate and sodium nitrate, and silver nitrate and lithium nitrate.

7. The low temperature autoignition composition of claim 4, wherein the silver nitrate oxidizer composition is a comelt consisting essentially of silver nitrate and potassium nitrate.

8. The low temperature autoignition composition of claim 6, wherein the powdered metal fuel is molybdenum.

9. The low temperature autoignition composition of claim 8, wherein the comelt is ground to a particle size of about 10 to about 30 microns, and the molybdenum powder has a particle size of less than about 6 microns.

10. The low temperature autoignition composition of claim 6, wherein

the mole fraction of silver nitrate in the comelt is about 0.4 to about 0.6;

the mole fraction of potassium nitrate in the comelt is about 0.6 to 0.4; and

the comelt is mixed with at least a stoichiometric amount of molybdenum powder fuel.

11. The low temperature autoignition composition of claim 10, wherein the autoignition temperature is about 130-135° C.

12. The low temperature autoignition composition of claim 1, wherein the silver nitrate oxidizer composition consists essentially of a mixture of silver nitrate and a solid organic nitrate or a solid organic nitrite.

13. The low temperature autoignition composition of claim 12, wherein the silver nitrate oxidizer composition consists essentially of a mixture of silver nitrate and guanidine nitrate.

14. The low temperature autoignition composition of claim 12, wherein the powdered metal fuel is selected from the group consisting of molybdenum, titanium, zirconium, niobium, nickel, chromium, zinc, aluminum, and cerium.

15. The low temperature autoignition composition of claim 12, wherein the powdered metal fuel is selected fuel from the group consisting of molybdenum, titanium, zirconium, zinc, and cerium.

16. The low temperature autoignition composition of claim 12, wherein the powdered metal fuel is molybdenum.

17. The low temperature autoignition composition of claim 16, wherein the molybdenum fuel is present in an amount greater than that required to form a mixture in which the amount of molybdenum fuel is stoichiometric relative to the silver nitrate oxidizer composition, thereby providing an autoignition composition having an autoignition temperature that is less than the autoignition temperature of a similar composition in which the amount of molybdenum fuel is stoichiometric relative to the silver nitrate oxidizer composition.

18. The low temperature autoignition composition of claim 1, further consisting essentially of an alkali metal chloride, alkali metal fluoride, alkali metal bromide, alkaline earth metal chloride, alkaline earth metal fluoride, or alkaline earth metal bromide.

19. The low temperature autoignition composition of claim 1, further consisting essentially of an output augmenting composition, consisting essentially of a metal in combination with an energetic oxidizer selected from the group consisting of ammonium perchlorate, alkali metal chlorates, alkali metal perchlorates, and alkali metal nitrates.

20. The low temperature autoignition composition of claim 1, wherein the silver nitrate oxidizer composition consists essentially of silver nitrate and a complex salt nitrate of at least one of  $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$  and  $\text{ZrO}(\text{NO}_3)_2$ .

21. The low temperature autoignition composition of claim 1, wherein the silver nitrate oxidizer composition

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consists essentially of silver nitrate and a dried hydrated metal nitrate of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  or  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ .

22. The low temperature autoignition composition of claim 1, further consisting essentially of a metal oxide catalyst.

23. The low temperature autoignition composition of claim 22, wherein the metal oxide catalyst is selected from the group consisting of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{CeO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{CrO}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CO}_3\text{O}_4$ ,  $\text{NiO}$ ,  $\text{CuO}$ ,  $\text{ZnO}$ ,  $\text{ZrO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{MoO}_3$ , and  $\text{Ag}_2\text{O}$ .

24. The low temperature autoignition composition of claim 1, wherein the fuel consists essentially of molybdenum and the silver nitrate oxidizer composition consists essentially of a mixture of silver nitrate, potassium nitrate, and guanidine nitrate.

25. A low temperature autoignition composition for safely initiating combustion of a main pyrotechnic charge in a gas generator or pyrotechnic device exposed to flame or a high temperature environment comprising:

a mixture of a silver nitrate oxidizer composition and a powdered metal fuel; wherein

the silver nitrate oxidizer composition comprises a mixture or a comelt comprising silver nitrate and at least one additional component selected from the group consisting of an alkali metal nitrate, an alkaline earth metal nitrate, a complex salt nitrate, a dried hydrated nitrate, silver nitrate, an alkali metal chlorate, an alkali metal perchlorate, an alkaline earth metal chlorate, an alkaline earth metal perchlorate, ammonium perchlorate, sodium nitrite, potassium nitrite, silver nitrite, a complex salt nitrite, a solid organic nitrate, and a solid organic nitrite;

the metal fuel is present in an amount at least substantially stoichiometric relative to the silver nitrate oxidizer composition; and

the mixture of metal fuel and silver nitrate oxidizer composition has a mix intimacy and homogeneity

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sufficient in the composition between the silver nitrate oxidizer composition and the metal fuel to react in an autoignition reaction of metal fuel and silver nitrate oxidizer composition at an autoignition temperature of no more than about  $232^\circ\text{C}$ ., thereby providing an autoignition composition having the autoignition temperature of no more than about  $232^\circ\text{C}$ .; wherein

heating the autoignition composition to the autoignition temperature results in a reaction between silver nitrate and the metal fuel, thereby initiating the autoignition reaction.

26. The low temperature autoignition composition of claim 25, wherein the metal fuel is present in an amount sufficient to form a fuel rich composition, thereby providing an autoignition composition having an autoignition temperature that is less than the autoignition temperature of a similar composition having a stoichiometric amount of metal fuel.

27. The low temperature autoignition composition of claim 26, wherein the powdered metal fuel is chosen from the group consisting of molybdenum, magnesium, calcium, strontium, barium, titanium, zirconium, vanadium, niobium, tantalum, chromium, tungsten, manganese, iron, cobalt, nickel, copper, zinc, cadmium, tin, antimony, bismuth, aluminum, and silicon.

28. The low temperature autoignition composition of claim 26, wherein the fuel comprises molybdenum and the silver nitrate oxidizer composition comprises silver nitrate, potassium nitrate, and guanidine nitrate.

29. The low temperature autoignition composition of claim 1, further consisting essentially of a solid organic amine.

30. The low temperature autoignition composition of claim 12, further consisting essentially of a solid organic amine.

31. The low temperature autoignition composition of claim 25, further comprising a solid organic amine.

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